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(54) **Coated SiO<sub>2</sub> particles**

(57) Spherical SiO<sub>2</sub> particles with a size of from 5 to 500 nm coated at individual points with TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub> particles with a size of less than 60 nm. The coated SiO<sub>2</sub> particles can be aftercoated with silanes or further metal oxides. The products obtained are used for pigmenting paints, printing inks, plastics and coatings or as sunscreen agents.

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## Description

The invention relates to spherical  $\text{SiO}_2$  particles coated with oxides of the elements titanium, iron or zircon, to a process for their preparation and to the use of the products obtained.

5 Spherical  $\text{SiO}_2$  particles are known per se from the prior art.  $\text{SiO}_2$  particles are obtained by hydrolytic polycondensation from alcoholate compounds, after which they are also obtained in the form of compact, monodisperse, spherical particles. The fundamental reaction conditions for the preparation of  $\text{SiO}_2$  particles by hydrolytic polycondensation can be found, for example, in the publications by W. Stöber et al. in J. Colloid and Interface Science 26, 62 (1968) and 30, 568 (1969) and in US Patent 3,634,588. The particles thus prepared, however, often show large standard deviations in  
10 their particle diameter and have a certain porosity.

For the preparation of highly monodisperse, non-porous, spherical  $\text{SiO}_2$  particles which have a standard deviation of not more than 5%, reference is made to EP 0 216 278, which discloses a correspondingly oriented preparation process based on hydrolytic polycondensation. The key feature of this process, which is preferred for the preparation of the particles according to the present invention, is a two-stage procedure. In this procedure, hydrolytic polycondensation of  
15 tetraalkoxysilanes in aqueous-alkaline-ammoniacal medium is first used to form a sol or a suspension of primary particles, which are then brought by metered addition of further tetraalkoxysilane to the desired final size.

An appropriate process for the preparation of various metal oxides in the form of spherical particles with narrow particle size distribution is to be found in EP 0 275 688.

A corresponding two-stage process for the preparation of various metal oxides and also mixed oxides, which, furthermore, also have glycolic groups chemically bonded to the surface, is described in EP 0 391 447.

$\text{SiO}_2$  particles organically modified in this way can be used as tailor-made sorbents for chromatography. They are particularly suitable for use in reversed-phase chromatography. The use of these particles allows the separation of high molecular weight biomolecules, such as peptides, proteins or nucleic acids.

The subsequent coating of spherical  $\text{SiO}_2$  particles with titanium dioxide is described in Japanese Published Specification No. 06-011 872.  $\text{SiO}_2$  particles with a size of 0.5-50  $\mu\text{m}$  are coated by suspending them in an aqueous titanyl sulfate solution and heating the suspension, the titanyl sulfate hydrolysing and the resulting titanium oxide hydrate being precipitated onto the  $\text{SiO}_2$  particles. In this process, the entire surface is coated with titanium dioxide. The weight ratio of silicon dioxide to titanium dioxide is within the range from 10:90 to 90:10.

The size of the individual crystallites within the continuous  $\text{TiO}_2$  coat is about 500 nm.

30 The coated  $\text{SiO}_2$  particles are separated off, washed and dried in accordance with known methods. In order to increase their mechanical strength they are heated at from 500 to 900°C for from 30 minutes to 5 hours.

The product obtained possesses a high masking capacity and a screening effect towards ultraviolet radiation. It is used in cosmetology as a component of make-up formulations.

The high masking capacity of this product makes it unsuitable for use in sunscreen compositions. A sunscreen composition should possess a high absorption and reflection capacity for ultraviolet radiation but at the same time should be highly transparent to the visible component of sunlight, so that it is not visible on the skin.

The object of the present invention is to provide a product which consists of spherical  $\text{SiO}_2$  particles coated at individual points with oxide particles of the elements titanium, iron or zircon. The product is to have a high absorption and reflection capacity for ultraviolet radiation while in contrast being highly transparent to visible light. Furthermore, the  
40 product should not have a tendency towards agglomeration, such a tendency being a known feature of conventional UV protection filters, for example ultrafine titanium dioxide.

A further object of the present invention is to provide a product which is suitable as filler in organic matrix materials, with the refractive index of the particles being adapted as a function of the application to the refractive index of the organic matrix.

45 It has, surprisingly, been found that, by means of a specific procedure, it is possible to coat spherical  $\text{SiO}_2$  particles with a size of from 5 to 500 nm at individual points with oxide particles of the elements titanium, iron or zircon with a size of less than 60 nm to give highly transparent products which possess a high absorption and reflection capacity in the ultraviolet region.

The invention therefore provides spherical  $\text{SiO}_2$  particles with a size of from 5 to 500 nm, preferably with a size of less than 100 nm, which are coated at individual points with oxide particles of the elements titanium, iron or zircon or mixtures of these methaloxydes with a size of less than 60 nm, which coated particles are obtainable for example by adding a from 5 to 40% titanium tetrachloride solution at a metering rate of from 0.0005 to 0.5 mg of  $\text{TiO}_2$  per minute and per  $\text{m}^2$  surface area of the  $\text{SiO}_2$  particles to an aqueous dispersion of the  $\text{SiO}_2$  particles at a pH of from 1.3 to 2.5, preferably from 1.6 to 2.0, separating off the coated  $\text{SiO}_2$  particles and subjecting them to drying and, if desired, calci-  
55 nation.

The invention additionally provides a process for the preparation of spherical  $\text{SiO}_2$  particles with a size of from 5 to 500 nm, preferably less than 100 nm, which are coated at individual points with oxide particles of the elements titanium, iron or zircon with a size of less than 60 nm, which is characterized in that the  $\text{SiO}_2$  particles are dispersed in deionized water at a temperature of from 50 to 90°C in a concentration of from 1 to 30% by weight, preferably 5-10% by weight,

in case of a coating with  $\text{TiO}_2$  particles an aqueous from 5 to 40% titanium salt solution is added at a pH of from 1.3 to 2.5, preferably from 1.6 to 2.0, at a metering rate of from 0.0005 to 0.5 mg of  $\text{TiO}_2$  per minute and per  $\text{m}^2$  surface area of the  $\text{SiO}_2$  particles, the pH being kept constant by simultaneous addition of a base, the coated  $\text{SiO}_2$  particles are separated off, washed with water and then with ethanol, are initially dried in air and are then dried in vacuo at from 70 to 125°C.

The invention also provides for the use of the particles according to the invention as sunscreen agents in cosmetic formulations and as filler in organic matrix materials. Furthermore they are used for pimenting paints, printing inks, plastics and coatings.

Specific embodiments of the invention are comprised in the subclaims.

The spherical  $\text{SiO}_2$  particles to be used as starting material are known per se from the prior art.

The fundamental reaction conditions for the preparation of  $\text{SiO}_2$  particles by hydrolytic polycondensation can be found, for example, in the publications by W. Stöber et al. in J. Colloid and Interface Science 26, 62 (1968) and 30, 568 (1969) and in US Patent 3,634,588. The particles thus prepared, however, often show large standard deviations in their particle diameter and have a certain porosity.

For the preparation of highly monodisperse, non-porous, spherical  $\text{SiO}_2$  particles which have a standard deviation of not more than 5%, reference is made to EP 0 216 278, which discloses a correspondingly oriented preparation process based on hydrolytic polycondensation. The key feature of this process, which is preferred for the preparation of the particles according to the present invention, is a two-stage procedure. In this procedure, hydrolytic polycondensation of tetraalkoxysilanes in aqueous-alkaline-ammoniacal medium is first used to form a sol or a suspension of primary particles, which are then brought by metered addition of further tetraalkoxysilane to the desired final size.

The grain size of the  $\text{SiO}_2$  particles to be employed as starting material is dependent on the intended use of the  $\text{SiO}_2$  particles according to the invention which are coated with oxide particles of the elements titanium, iron and zircon.

Particle sizes of between 5 nm and 500 nm are available. For the use of the products according to the invention as sunscreen agents in cosmetic formulations, for example, particle sizes of from 5 to 100 nm are employed.

For the use as filler in organic matrix materials, particle sizes of from 50 to 500 nm are employed. Depending on the choice of the oxides on which the inorganic particles are based, the refractive index of the products according to the invention can be tailored precisely to the refractive index of the organic matrix. Polymers or polymerizable systems comprising these particles can be used, for example, as embedding compositions for optical, electrooptical and optoelectrical components. Such embedding compositions exhibit an improved optical homogeneity. Light-emitting diodes produced with such compositions are distinguished inter alia by an enhanced light yield. Further details on this use of the products according to the invention are given in WO 93/25611.

The size of the  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{ZrO}_2$  particles in the products according to the invention is below 60 nm.

The proportion of titanium dioxide, iron oxide or zircon oxide in the product according to the invention is from 20 to 75% by weight, preferably from 40 to 50% by weight.

The coated  $\text{SiO}_2$  particles according to the invention are also produced on the following way: An aqueous solution of a metal salt, e.g. titanium tetrachloride, is heated to 60 °C with stirring. The obtained suspension of the metal oxide is added dropwise to a suspension of spherical  $\text{SiO}_2$  particles. The pH is adjusted to 2.0 with 32 % NaOH solution with stirring and a silane coupling agent is added to the suspension. After 15 minutes the pH value is increased to 8.0 with 32 % NaOH solution and the suspension is stirred again for 10 minutes. After filtering, washing and drying the coated  $\text{SiO}_2$  particles are powdered by using a blender and the obtained powder is calcinated at 700 °C for 5 minutes.

The products according to the invention can be aftercoated with organic and inorganic compounds by known methods.

By aftercoating with silanes or metal oxides it is possible to prevent the agglomeration of the monodisperse particles during the drying process. In the case where the products according to the invention are used as sunscreen agents, it is possible by aftercoating with iron oxide to adjust the colour to a defined skin shade. Aftercoating with zinc oxide increases the effectiveness of the product as a UV-A absorber.

When aftercoating with a silane of the general formula  $\text{R}_n\text{Si}(\text{OX})_3$ , in which  $\text{R}_n$  is an alkyl group having 1 to 18 carbon atoms and X is an alkyl group having 1 or 2 carbon atoms, from 0.02 to 2% by weight of the silane, calculated as  $\text{SiO}_2$ , are applied to the product according to the invention. Preference is given to the use of  $\text{CH}_3\text{Si}(\text{OMe})_3$ .

Preferred metal oxides used for aftercoating are zinc oxide, iron oxide, zirconium oxide and cerium oxide.

From SEM micrographs of the products according to the invention with two different particle sizes, 250 and 50 nm, it is evident that the titanium dioxide is arranged at individual points on the surface of the  $\text{SiO}_2$  particles and does not form, as is the case with known products, for example according to JP 06-011 872 (Kokoku), a continuous coat.

The concentration of the additionally applied metal oxides is from 1 to 100% by weight, preferably 10% by weight, based on the content of  $\text{TiO}_2$ .

For the process according to the invention for the preparation of the  $\text{SiO}_2$  particles coated at individual points with  $\text{TiO}_2$  particles, it is essential to avoid an excess of titanium salt. This is achieved in that the quantity of titanium salt supplied to the hydrolysis per unit time is only that necessary for uniform formation of the  $\text{TiO}_2$  particles. This effect is best achieved if the hydrolysis is carried out at a temperature which is as constant as possible and with approximately con-



stant pH.

The from 5 to 40% titanium tetrachloride solution is added at a metering rate of from 0.0005 to 0.5 mg of  $\text{TiO}_2$  per  $\text{m}^2$  surface area of the  $\text{SiO}_2$  particles per minute to an aqueous dispersion of the  $\text{SiO}_2$  particles at a pH of from 1.3 to 2.5, preferably from 1.6 to 2.0.

Since the different fractions of  $\text{SiO}_2$  particles possess different diameters and therefore different surface areas, the values are different for each particle size when equal quantities are employed.

Particle $\varnothing$ in nm	Surface area $\text{m}^2/\text{g}$	Min. quantity of $\text{TiO}_2$ per $\text{m}^2$ per minute	Max. quantity of $\text{TiO}_2$ per $\text{m}^2$ per minute
1000	3	0.02 mg	0.5 mg
500	6	0.01 mg	0.25 mg
250	12	0.005 mg	0.15 mg
100	30	0.002 mg	0.05 mg
50	60	0.001 mg	0.025 mg
25	120	0.0005 mg	0.012 mg

The  $\text{TiCl}_4$  solution used preferably has a concentration of 15% by weight of  $\text{TiCl}_4$  with a density of 1.123 g/ml. The concentration range of the  $\text{TiCl}_4$  solutions to be used extends from 5 to 40% by weight.

In accordance with the process of the invention, it is possible to offer the surfaces to be coated, per unit time, only a small quantity of titanium salt such that all of the titanium dioxide hydrate is able to deposit on the surfaces, and no freely mobile by-products can be formed in the dispersion. Further details are described in US 3,553,001.

The  $\text{SiO}_2$  particles according to the invention, coated with titanium dioxide, iron oxide or zircon oxide, can, depending on their intended use, be coated with further metal oxides or with organic compounds, for example silanes, by known methods.

Coating with zinc oxide is likewise carried out by known methods. The zinc oxide hydrate is precipitated by hydrolysis of zinc chloride using an ammonium complex at a pH of from 11 to 12. The  $\text{SiO}_2$  particles according to the invention which are coated with  $\text{TiO}_2$  particles are suspended at room temperature in deionized water, the pH is adjusted to 11 - 12 with ammonia solution, and a prepared zinc chloride solution is then added. By slow heating of the suspension the ammonia is driven off, the pH of the suspension falls and the zinc oxide hydrate is slowly precipitated. The particles coated with zinc oxide hydrate are separated off, washed with water and then with ethanol, initially dried in air and then dried in vacuo at from 70 to 125°C.

The zinc oxide hydrate can also be precipitated by hydrolysing zinc oxalate or zinc chloride.

Aftercoating of the particles according to the invention with iron (III) oxide is likewise carried out by known methods; the same applies to aftercoating with zirconium oxide.

In the case of aftercoating with iron (III) oxide, an iron(III) chloride solution is metered at a temperature of from 60 to 90°C and at a pH of from 2.5 to 4.5 into an aqueous suspension of the  $\text{SiO}_2$  particles according to the invention, coated with titanium dioxide. The pH is kept constant by simultaneous addition of 32% sodium hydroxide solution.

The particles coated with iron(III) oxide are separated off, washed with water and then with ethanol, initially dried in air and then dried in vacuo at from 70 to 125°C.

The pigments according to the invention are dried at temperatures from 110 to 125 °C under normal pressure or from 70 to 125 °C in vacuo. Dependent on the purpose the pigments can be additionally calcined at temperatures from 300 °C to 900 °C for from 5 to 60 minutes.

The pigments according to the invention are used for pigmenting paints, printing inks, plastics, coatings or as sunscreen agent in cosmetic formulations.

When the pigment according to the invention is used as sunscreen agent in cosmetic formulations, the pigment is incorporated into the formulation in a concentration of up to 5% by weight.

Figure 1 compares two embodiments of the pigment according to the invention with known sunscreen agents with respect to their transparency in the wavelength range from 220 to 800 nm. For this comparison, the products were incorporated into VS medium of Dainichiseika Co. Ltd. in a concentration of 1.5% by weight, and the transparency was measured.

The VS medium contains a copolymer of vinyl chloride and vinyl acetate as main resin and xylene in a concentration of from 30 to 40 % and cyclohexanone in a concentration of from 50 to 60 %

Plot 1 shows the transparency of an ultrafine titanium dioxide, while plot 2 shows the transparency of an ultrafine

titanium dioxide coated with iron oxide. Plot 3 shows the transparency of a pigment according to the invention having the composition 27% SiO<sub>2</sub>, 53% TiO<sub>2</sub>, 20% Fe<sub>2</sub>O<sub>3</sub>. Plot 4 shows the transparency of a pigment according to the invention having the composition 31% SiO<sub>2</sub> and 69% TiO<sub>2</sub>.

The plots show that, in the region of visible light, the pigments according to the invention possess a substantially higher transparency than ultrafine titanium dioxide. This means that ultrafine titanium dioxide causes a white film to appear on the hand, whereas the pigments according to the invention remain invisible on the skin owing to their high transparency.

Table 1 compares the transparency and absorbance of the 4 abovementioned pigments at identical and at different concentrations in the formulation.

Table 1

Pigment No.	Concentr % by weight	Transmittance (%)			Absorbance	
		Visible light	UV-A	UV-B	UV-A	UV-B
		(550 nm)	(380 nm)	(300nm)	(380nm)	(300 nm)
1	1.5	22	1	0	2.0	3.7
2	1.5	76	34	0	0.5	2.7
3	1.5	49	6	0	1.2	3.0
4	1.5	75	19	0	0.7	2.8
5	0.75	66	12	1	0.9	2.0
6	3.0	64	12	0	0.9	3.4
7	1.0	63	17	2	0.7	1.7
8	2.0	62	8	0	1.2	3.3
Pigments Nos. 1 and 5: Ultrafine TiO <sub>2</sub> Pigments Nos. 2 and 6: Invention (31% SiO <sub>2</sub> , 69% TiO <sub>2</sub> ) Pigments Nos. 3 and 7: Ultrafine TiO <sub>2</sub> + Fe <sub>2</sub> O <sub>3</sub> Pigments Nos. 4 and 8: Invention (27% SiO <sub>2</sub> , 53% TiO <sub>2</sub> , 20% Fe <sub>2</sub> O <sub>3</sub> )						

The table shows that pigment No. 2 according to the invention possesses a transparency at 550 nm which is approximately 3.5 times higher than the transparency of ultrafine titanium dioxide (pigment No. 1).

To establish approximately the same transparency, relative to ultrafine titanium dioxide, 4 times the quantity of the pigment according to the invention can be added to a cosmetic formulation. This means that, with the pigment according to the invention, it is possible to achieve a markedly higher light protection effect.

Figure 2 compares two embodiments of the pigment according to the invention with a known sunscreen agent (ultrafine TiO<sub>2</sub>) with respect to their extinction in the wavelength range from 200 to 400 nm. The SiO<sub>2</sub> particles coated with TiO<sub>2</sub> (particles sizes 25 and 50 nm) show a significantly higher extinction (shielding capability) in the wavelength range from 200 to 320 nm. However, in the range of the visible light the pigments of the invention show the same extinction (transparency) as the ultrafine TiO<sub>2</sub>.

According to the invention SiO<sub>2</sub> as a core particle for newly pigments is coated with TiO<sub>2</sub> particles. Due to TiO<sub>2</sub> particles contact the core SiO<sub>2</sub> particles directly, TiO<sub>2</sub> particles can perform as if they were single particle keeping. Thereby this fine particle of TiO<sub>2</sub> coated SiO<sub>2</sub> pigment has superior transmittance and great UV ray shielding capability. This newly developed pigment can be possible to contain highly in a sunscreen products because of those superior transparency, so it will be able to make the excellent sunscreen which has high UV-ray shielding capability.

In addition, the Fe<sub>2</sub>O<sub>2</sub> type pigment is treated with iron oxide on the surface of TiO<sub>2</sub> coated colloidal silica particles. For UV-A&B range Fe<sub>2</sub>O<sub>2</sub> has also shielding capability, so this iron oxide type pigment has higher UV-A&B shielding capability compared with TiO<sub>2</sub> type pigment because of the efficacy of combination TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>2</sub>. With the addition the pigment coloring to skin-tone can be get by the content of iron oxide. Sunscreen products with several skin tone in cosmetics can be

produced. The examples which follow are intended to describe the invention in more detail without limiting it.

Example 1

3000 g of an aqueous dispersion of  $\text{SiO}_2$  particles with a size of 250 nm (5% by weight  $\text{SiO}_2$ ) are heated to 75°C with stirring. 198 g of 60%  $\text{TiCl}_4$  solution are diluted with 141 g of deionized water and metered at a metering rate of 1.5 ml/min into the dispersion. By simultaneous addition of 32% NaOH solution, the pH is kept constant at 2.2. After 60 minutes, the metering rate of the  $\text{TiCl}_4$  solution is increased to 3 ml/min. Metered addition of the  $\text{TiCl}_4$  solution is complete after 110 minutes. The reaction mixture is then stirred for a further 15 minutes and neutralized with NaOH solution, and the solid is separated off, washed free from salt, then washed with 0.5 l of ethanol and, after initial drying in air, is dried overnight in a vacuum drying cabinet at from 70 to 75°C. The  $\text{TiO}_2$  content of the pigment is 25% by weight.

Example 2

3000 g of an aqueous dispersion of  $\text{SiO}_2$  particles with a size of 250 nm (5% by weight  $\text{SiO}_2$ ) are heated to 75°C with stirring. 350 g of iron(III) chloride solution (15% by weight Fe, Merck Art. 5513) are diluted with 306 g of deionized water to an iron content of 8% by weight. The solution is metered into the dispersion at 0.5 ml/min. After 10 minutes, the rate is increased to 1.0 ml/min and, after a further 10 minutes, to 1.5 ml/min. This rate is maintained until the end of coating. By simultaneous addition of 32% sodium hydroxide solution, the pH is kept constant at between 3.2 and 3.3. Addition is complete after about 6 hours. After the end of the addition of  $\text{FeCl}_3$ , stirring is continued for 15 minutes and the mixture is then neutralized with the NaOH solution. The solid is separated off, washed free from salt, washed with 0.5 l of ethanol and finally, after initial drying in air, is dried overnight in a vacuum drying cabinet at 70-75°C. The  $\text{Fe}_2\text{O}_3$  content of the finished pigment, based on oxides ( $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ ), is 33% by weight.

Example 3

$\text{SiO}_2$  particles with a size of 250 nm are coated with  $\text{TiO}_2$  in accordance with Example 1. The dispersion is then adjusted to a pH of 3.2 using NaOH solution. 11.5 g of iron(III) chloride solution (15% by weight Fe, Merck Art. 5513) are diluted with 46.9 g of water to an iron content of 3% by weight and metered at a rate of 0.5 ml/min into the above-mentioned dispersion. After 60 minutes, the rate of metering is increased to 1.0 ml/min. Addition is complete after about 90 minutes. During the addition of the iron chloride solution, the pH is held between 3.2 and 3.3 by simultaneous addition of NaOH solution. The reaction mixture is then stirred for a further 15 minutes and neutralized with NaOH solution, and the solid is separated off, washed free from salt, then washed with 0.5 l of ethanol and, after initial drying in air, is dried overnight in a vacuum drying cabinet at from 70 to 75°C. The iron content of the pigment is 5% by weight  $\text{Fe}_2\text{O}_3$ , based on the  $\text{TiO}_2$  content of the pigment.

Example 4

2400 g of an aqueous dispersion of  $\text{SiO}_2$  particles with a size of 250 nm (5% by weight  $\text{SiO}_2$ ) are heated to 75°C with stirring. 160 g of 60%  $\text{TiCl}_4$  solution are diluted with 112 g of deionized water, and 6.8 g of zinc chloride are added to the solution with stirring and dissolved. This solution is metered at a rate of 1.2 ml/min into the abovementioned dispersion, the pH being kept constant at from 2.2 to 2.3 by simultaneous addition of NaOH solution. After 60 minutes, the rate of metering is increased to 2.4 ml/min. Addition is complete after about 110 minutes. The reaction mixture is subsequently stirred for a further 15 minutes and neutralized over the course of 25 minutes with the aid of an NaOH solution. To ensure complete precipitation of the zinc hydroxide, the dispersion is subsequently stirred for 30 minutes and then allowed to cool to room temperature. The solid is then separated off, washed free from salt, then washed with 0.5 l of ethanol and, after initial drying in air, is dried overnight in a vacuum drying cabinet at from 70 to 75°C. The zinc oxide content of the pigment is 10% by weight, based on the  $\text{TiO}_2$  content of the pigment.

Example 5

2400 g of an aqueous dispersion of  $\text{SiO}_2$  particles with a size of 250 nm (5% by weight  $\text{SiO}_2$ ) are heated to 75°C with stirring. 160 g of 60%  $\text{TiCl}_4$  solution are diluted with 112 g of deionized water and metered at a rate of 1.2 ml/min into the abovementioned dispersion, the pH being kept constant at from 2.2 to 2.3 by simultaneous addition of NaOH solution. After 60 minutes, the rate of metering is increased to 2.4 ml/min. Addition is complete after about 110 minutes. The reaction mixture is subsequently stirred for a further 15 minutes and neutralized over the course of 25 minutes with the aid of an NaOH solution. Subsequently, a zinc chloride solution and an oxalic acid solution are metered, simultaneously but separately from one another, each at a rate of 1.2 ml/min into the neutralized reaction mixture, the pH being kept constant at 7 by simultaneous addition of an NaOH solution. The zinc chloride solution contains 6.8 g of zinc chloride in 61 g of water. The oxalic acid solution contains 6.3 g of oxalic acid in 61 g of water. Addition is complete after about 55 minutes. To ensure complete precipitation of the zinc oxide, the dispersion is subsequently stirred and then



allowed to cool to room temperature. The solid is separated off, washed free from salt, then washed with 0.5 l of ethanol and, after initial drying in air, is dried overnight in a vacuum drying cabinet at from 70 to 75°C. The zinc oxide content of the pigment is 10% by weight, based on the TiO<sub>2</sub> content of the pigment.

5 Example 6

3000 g of an aqueous dispersion of SiO<sub>2</sub> particles with a size of 250 nm (5% by weight SiO<sub>2</sub>) are heated to 75°C with stirring.

198 g of 60% TiCl<sub>4</sub> solution are diluted with 142 g of deionized water and metered at a metering rate of 1.5 ml/min into the dispersion. By simultaneous addition of 32% NaOH solution, the pH is kept constant at 2.2. After 60 minutes, the metering rate of the TiCl<sub>4</sub> solution is increased to 3 ml/min. Metered addition of the TiCl<sub>4</sub> solution is complete after 110 minutes. The reaction mixture is then stirred for a further 15 minutes and neutralized with NaOH solution.

Using 25% ammonia solution, the pH of the dispersion is adjusted to 11 - 12, and a zinc chloride solution consisting of 8.4 g of zinc chloride in 162 g of deionized water is added. By slow heating of the dispersion, the ammonia is driven off and the zinc hydroxide is precipitated. The precipitation end point is reached when the addition of dilute hydrochloric acid to a filtered sample of the dispersion no longer produces a precipitate. After cooling to room temperature, the solid is worked up in accordance with Example 5.

The zinc oxide content of the pigment is 10% by weight, based on the TiO<sub>2</sub> content.

20 Example 7

66 g (20 g as SiO<sub>2</sub>) of colloidal silica sol, type ST-S, with a size distribution of 5 to 9 nm in 500 ml of deionized water are heated to 80°C with stirring. The pH is rapidly adjusted to 1.6 with conc. HCl. Then 256 ml (45 g as TiO<sub>2</sub>) of TiCl<sub>4</sub> solution (418 g/l) are metered in over about 7 hours, while maintaining the pH at 1.6 using 32% NaOH solution. After stirring the suspension for 15 minutes, the pH is adjusted to 3.0 with 32% NaOH, and 3.3 g of silane coupling agent, CH<sub>3</sub>Si(OMe)<sub>3</sub>, in 50 ml of deionized water are fed into the reactor, and the suspension is held for 15 minutes. The pH is increased to 8.0 with 32% NaOH and the suspension is stirred again for 10 minutes. After filtering, washing and drying, the pigment (5 g) is calcined at a temperature of 700°C for 5 minutes.

30 Example 8

The reaction process is the same as in Example 7 until the step of metered addition of TiCl<sub>4</sub>. At this point, the pH is adjusted to 1.9 using 32% NaOH, and a solution of 33 g of FeCl<sub>3</sub>·6H<sub>2</sub>O in 100 ml of deionized water is metered in over 2 hours, maintaining a pH of 1.9 using 32% NaOH solution. After stirring the suspension for 15 minutes, the pH is adjusted to 3.0 with 32% NaOH, and then 4.2 g of silane coupling agent in 50 ml of deionized water are fed into the reactor. The suspension is held for 15 minutes. The pH is increased to 8.0 with 32% NaOH and the suspension is stirred again for 10 minutes. After filtering, washing and drying, the pigment (5 g) is calcined at a temperature of 700°C for 5 minutes.

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Example 9

Sunscreen cream

Raw Materials		
A:	Liquid paraffin	38.0 %
	Cetanol	1.5
	Beeswax	6.0
	Stearic acid	20.0
	POE (5,5) Cetyl ether	1.5
	Sorbitan monostearate	2.5
B:	10 % NaOH	1.0
	DI-water	31.5
C:	Glycerin	6.0
	TiO <sub>2</sub>	5.0
	SiO <sub>2</sub> coated TiO <sub>2</sub>	5.0

Preparation

TiO<sub>2</sub> and SiO<sub>2</sub> coated TiO<sub>2</sub> are dispersed in glycerin. A and B group are heated up seperately at 75 °C, then the two mixtures are emulsified by high speed stirring. Lastly, mix the C group is mixed with emulsified A & B mixture at 50 °C.

Example 10

An aqueous solution of titanium tetrachloride prepared from 50 ml of titanium tetrachloride and 500 ml of water (2,18 mol/l TiO<sub>2</sub>) is heated to 60 °C with stirring. To the white TiO<sub>2</sub> suspension obtained is added dropwise 40 g (12 g as SiO<sub>2</sub>) of colloidal silica sol, type XL, with a size distribution of 40 to 50 nm. The pH is increased to 2.0 with 32 % NaOH solution with stirring, and 2 g of CH<sub>3</sub>Si(OMe)<sub>2</sub> (silane coupling agent) in 50 ml of deionized water are added into the suspension, and the suspension is held for 15 minutes. The pH is increased to 8,0 with 32 % NaOH solution and the suspension is stirred again for 10 minutes. After filtering, washing and drying the dried product is powdered by using a blender and the resulting powder (5 g ) is calcined at 700 °C for 5 minutes.

Claims

1. Spherical SiO<sub>2</sub> particles with a size of from 5 to 500 nm coated at individual points with metal oxide particles with a size of less than 60 nm.
2. SiO<sub>2</sub> particles according to Claim 1, characterized in that the metal oxide is TiO<sub>2</sub>, Fe<sub>2</sub>O, ZrO<sub>2</sub> or mixtures of these metal oxides.
3. SiO<sub>2</sub> particles according to Claims 1 and 2, characterized in that the metal oxide content is from 20 to 75% by weight.
4. SiO<sub>2</sub> particles according to at least one of Claims 1 to 3, characterized in that the SiO<sub>2</sub> particles coated with metal oxides are aftercoated with inorganic and/or organic compounds.
5. SiO<sub>2</sub> particles according to Claim 4, characterized in that the organic compounds are silanes of the general formula R<sub>n</sub>Si(OX)<sub>3</sub>, in which R<sub>n</sub> is an alkyl group having 1 to 18 carbon atoms and X is an alkyl group having 1 or 2 carbon



atoms.

6. SiO<sub>2</sub> particles according to Claim 5, characterized in that the silane is CH<sub>3</sub>Si(OMe)<sub>3</sub>.
- 5 7. SiO<sub>2</sub> particles according to Claim 4, characterized in that the inorganic compounds are metal oxides.
8. SiO<sub>2</sub> particles according to Claim 7, characterized in that the metal oxides are zinc oxide, iron oxide or zirconium oxide.
- 10 9. Process for the preparation of spherical SiO<sub>2</sub> particles with a size of from 5 to 500 nm which are coated at individual points with metal oxide particles with a size of less than 60 nm, where an aqueous solution of titanium tetrachloride is heated to 60 °C with stirring, the obtained TiO<sub>2</sub> suspension is added dropwise to a suspension of spherical SiO<sub>2</sub> particles, the pH is adjusted to 2,0 with 32 % NaOH solution with stirring and a silane coupling agent is added to the suspension, after 15 minutes the pH value is increased to 8,0 with 32 % NaOH solution and the suspension is stirred again for 10 minutes, after filtering, washing and drying the coated SiO<sub>2</sub> particles are powdered by using a blender and the obtained powder is calcined at 700 °C for 5 minutes.
- 15 10. Process for the preparation of spherical SiO<sub>2</sub> particles with a size of from 5 to 500 nm which are coated at individual points with TiO<sub>2</sub> particles with a size of less than 60 nm, where spherical SiO<sub>2</sub> particles are dispersed in deionized water at a temperature of from 50 to 90°C in a concentration of from 1 to 30% by weight, an aqueous 5 to 40% titanium salt solution is added at a pH of from 1.3 to 2.5 at a metering rate of from 0.0005 to 0.5 mg of TiO<sub>2</sub> per minute and per m<sup>2</sup> surface area of the SiO<sub>2</sub> particles, the pH being kept constant by simultaneous addition of a base, the coated SiO<sub>2</sub> particles are separated off, washed with water and then with ethanol, are initially dried in air and are then dried in vacuo at from 70 to 125°C, and then, if desired, are calcined.
- 20 11. Process according to Claim 10, characterized in that the coated SiO<sub>2</sub> particles are calcined at 300-900°C for from 5 to 60 minutes.
- 25 12. Process according to Claims 10 and 11, characterized in that the SiO<sub>2</sub> particles coated with metal oxides, without intermediate drying or thereafter, are aftercoated with inorganic and/or organic compounds.
- 30 13. Process according to at least one of Claims 10 to 12, characterized in that the organic compounds used are silanes of the general formula R<sub>n</sub>Si(OR)<sub>3</sub>, in which R<sub>n</sub> is an alkyl group having 1 to 18 carbon atoms and R is an alkyl group having 1 or 2 carbon atoms.
- 35 14. Process according to Claim 13, characterized in that the silane used is CH<sub>3</sub>Si(OMe)<sub>3</sub>.
15. Process according to Claim 12, characterized in that the inorganic compounds used are metal oxides.
- 40 16. Process according to Claim 15, characterized in that the metal oxides are zinc oxide, iron oxide or zirconium oxide.
17. Use of the SiO<sub>2</sub> particles according to at least one of Claims 1 to 8 for pigmenting paints, printing inks, plastics and coatings or as sunscreen agents.
- 45 18. Cosmetic formulation comprising SiO<sub>2</sub> particles according to at least one of Claims 1 to 8 in a proportion of up to 5% by weight.

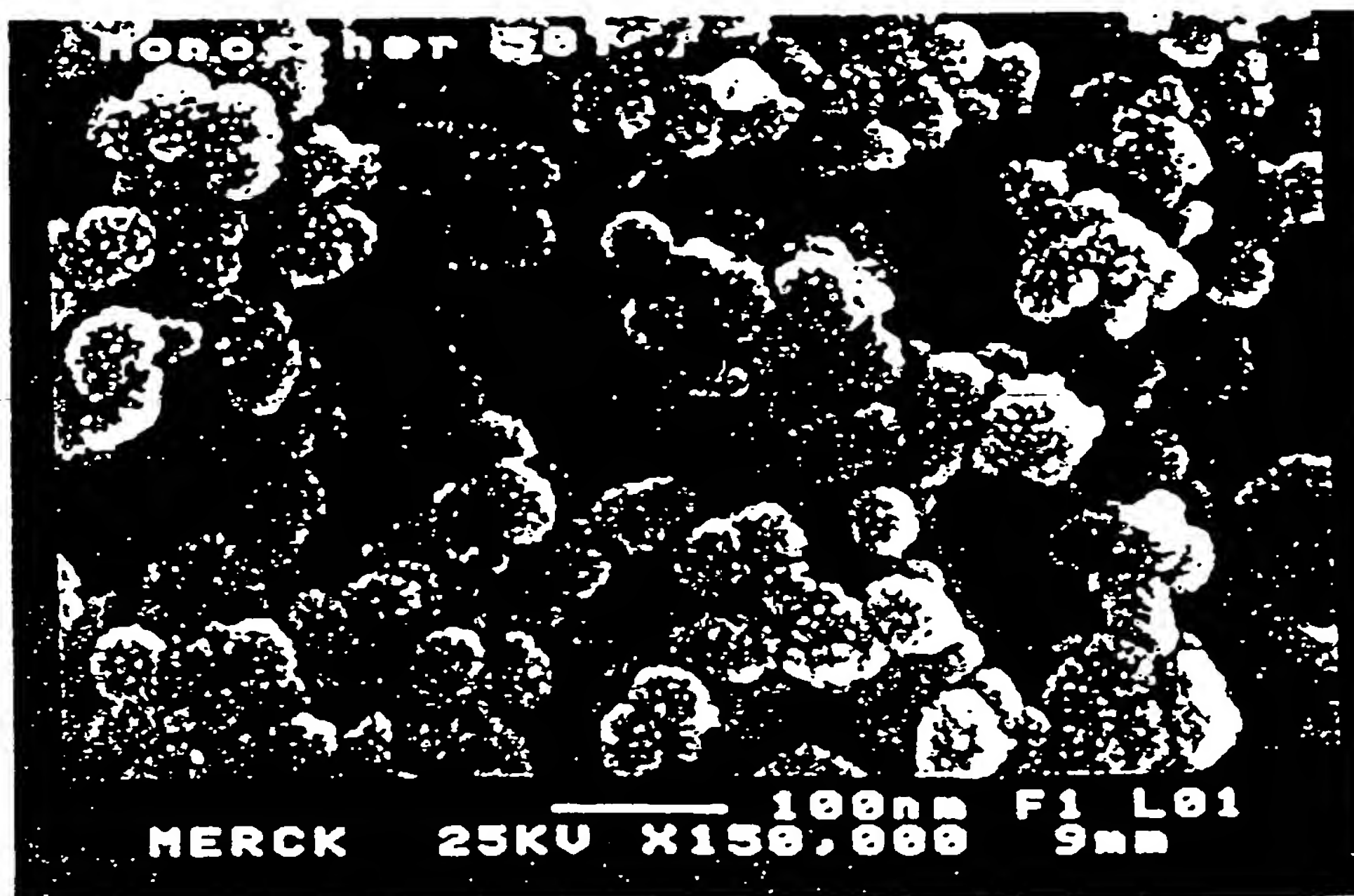
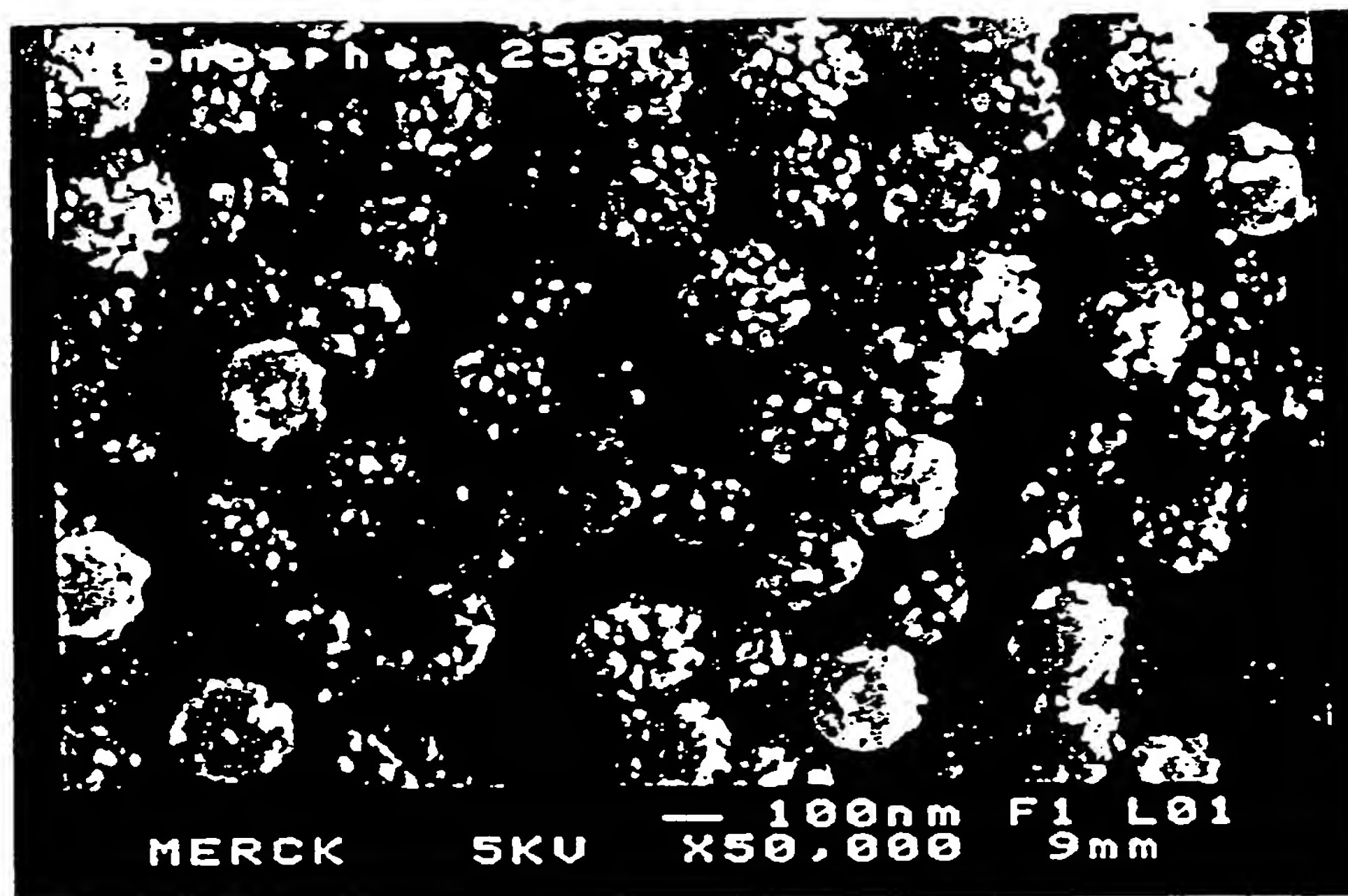


Figure 1

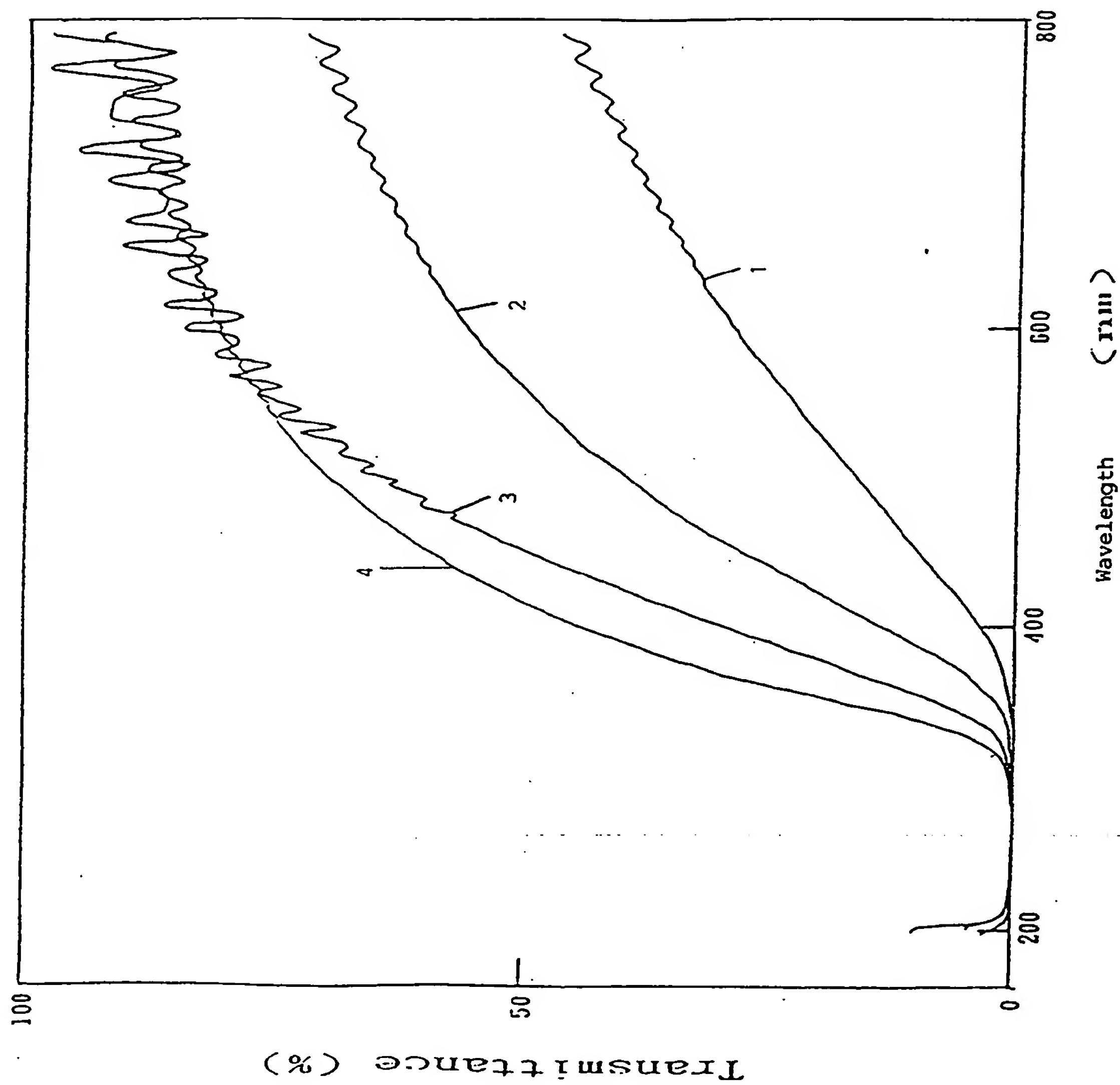
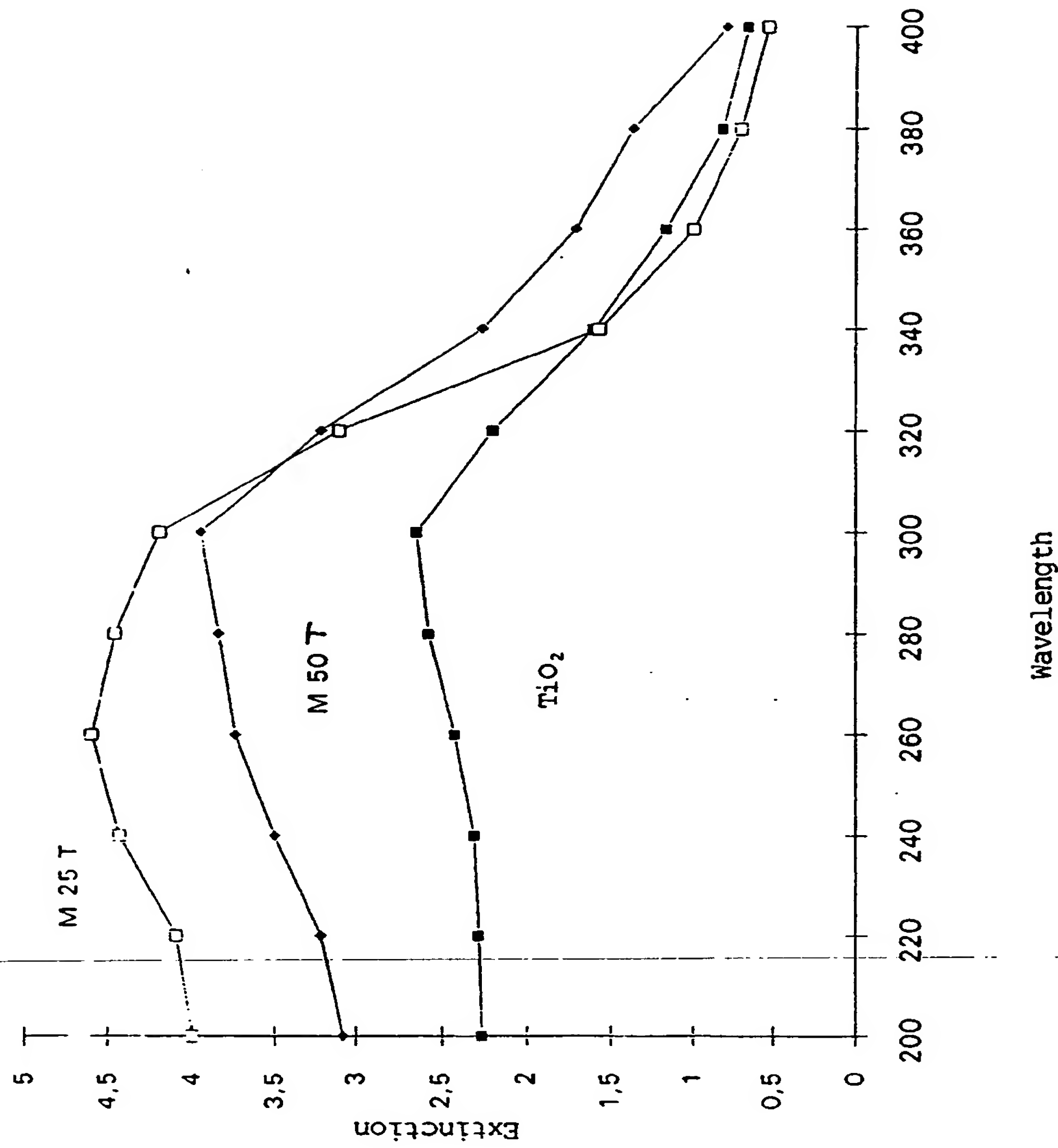
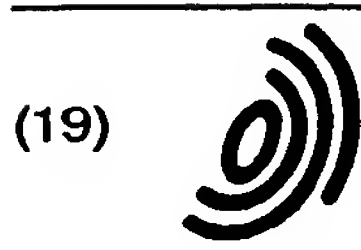




Figure 2





(19)

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**(54) Coated SiO<sub>2</sub> particles**

(57) Spherical SiO<sub>2</sub> particles with a size of from 5 to 500 nm coated at individual points with TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub> particles with a size of less than 60 nm. The coated SiO<sub>2</sub> particles can be aftercoated with silanes or further metal oxides. The products obtained are used for pigmenting paints, printing inks, plastics and coatings or as sunscreen agents.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 97 10 5916

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 512 094 A (HOWARD R.) 30 April 1996 * column 6, line 17-22; claims 1,2,9,11 *	1-3,10,11,17	C09C1/30 C09C3/06 C09C3/12 C09D7/12
A	EP 0 172 730 A (E.I. DU PONT DE NEMOURS) 26 February 1986 * claims 1,5; examples 1,2 *	1-5,9-12	C09D11/00 C08K9/02 C08K9/06 A61K7/42 A61K7/00
D,A	DATABASE WPI Week 8618 Derwent Publications Ltd., London, GB; AN 86-116717 XP002105634 & JP 61 057653 A (NIPPON MENARD TESHOHIN ET AL.), 24 March 1986 * abstract *	1-3,10,17,18	
A	EP 0 778 319 A (OJI PAPER COMPANY) 11 June 1997 * claims 1,7 *	1-3,10	
A	DATABASE WPI Week 9118 Derwent Publications Ltd., London, GB; AN 91-130214 XP002105635 & JP 03 070768 A (TORAY IND.) , 26 March 1991 * abstract *	1,2,17	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C09C A61K
A	DATABASE WPI Week 9340 Derwent Publications Ltd., London, GB; AN 93-317707 XP002105636 & JP 05 230394 A (KAO), 7 September 1993 * abstract *	1,2,4,7,8,17	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 June 1999	Examiner Van Bellinghen, I
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 97 10 5916

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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11-06-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5512094 A	30-04-1996	NONE	
EP 172730 A	26-02-1986	US 4600646 A	15-07-1986
		CA 1247073 A	20-12-1988
		DE 3566658 A	12-01-1989
		DK 369985 A	16-02-1986
		GR 851982 A	13-12-1985
		JP 1057046 B	04-12-1989
		JP 1571080 C	25-07-1990
		JP 61058811 A	26-03-1986
EP 778319 A	11-06-1997	JP 9156919 A	17-06-1997
		CA 2191932 A	09-06-1997

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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